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2019-04-25

Gomez Millan , G , Hellsten , S , King , A W T , Pokki , J-P , Llorca , J & Sixta , H 2019 , ' A comparative study of water-immiscible organic solvents in the production of furfural from xylose and birch hydrolysate ' , Journal of Industrial and Engineering Chemistry , vol. 72 , pp. 354-363 . <https://doi.org/10.1016/j.jiec.2018.12.037>

<http://hdl.handle.net/10138/307298>

<https://doi.org/10.1016/j.jiec.2018.12.037>

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A comparative study of water-immiscible organic solvents in the production of furfural from xylose and birch hydrolysate

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Abstract

Furfural (FUR) was produced from xylose using a biphasic batch reaction system. Water-immiscible organic solvents such as isophorone, 2-methyltetrahydrofuran (2-MTHF) and cyclopentyl methyl ether (CPME) were used to promptly extract FUR from the aqueous phase in order to avoid the degradation to humins as largely as possible. The effect of time, temperature, organic solvent and organic-to-aqueous ratio on xylose conversion and FUR yield were investigated in auto-catalyzed conditions. Experiments at three temperatures (170, 190 and 210 °C) were carried out in a stirred microwave-assisted batch reactor, which established the optimal conditions for achieving the highest FUR yield. The maximum FUR yields from xylose were 78 mol% when using CPME, 48 mol% using isophorone (due to its phase-behavior nature) and 71 mol% in the case of 2-MTHF at an aqueous to organic phase ratio of 1:1. Birch hydrolysate was also used to show the high furfural yield that can be obtained in the biphasic system under optimized

conditions. The present study suggests that CPME can be used as a green and efficient extraction solvent for the conversion of xylose into furfural without salt addition.

Keywords: xylose, furfural, prehydrolyzate liquor, 2-MTHF, CPME, isophorone

Introduction

Hemicellulose, one of the three major components in lignocellulosic biomass including cellulose and lignin, is a cross-linked fibrous amorphous heteropolysaccharide, consisting mostly of different pentoses (C_5) with some hexoses and uronic acids sugar monomers [1]. Hemicelluloses are the second most abundant natural polymer [2]. The main C_5 sugars found in hemicellulose are xylose and arabinose. Xylan, which is degraded during kraft pulping of hardwood, is currently valorized to sugar-based products in very small quantities. In these cases, xylan is typically hydrolysed to xylose and then further reduced to xylitol. In a typical hardwood kraft pulping process, about 50% of the xylan in the wood is degraded to carboxylic acids, which are enriched in the black liquor together with the degraded lignin. After thermal concentration to thick liquor, the organic matter is burnt and the energy obtained is used for the pulping process [3]. Therefore, valorization of these attractive industrial streams extends the possibility to create new markets and new economic models.

According to the United States Department of Energy, furfural (furan-2-carbaldehyde, FUR) is one of the top 10 most rewarding bio-based platform molecules [4]. FUR is industrially produced by the dehydration of xylose and other C_5 -sugars in aqueous solutions usually found in hemicellulosic fractions of lignocellulosic biomass. The FUR application range varies from the chemical industry, where it is used as solvent and extracting agent, to the agrochemical sector, where it is employed as nematicide,

fungicide and herbicide; it can also be involved in processes in the pharmaceutical and cosmetic industries [5]. Furthermore, FUR serves as a platform molecule to produce furfuryl alcohol (via hydrogenation) [6,7] with applications in the food industry as flavoring agent, for the synthesis of furan resins and in the biofuel sector. Other important molecules that can be potentially synthesized from FUR are: tetrahydrofurfuryl alcohol, furan as a diene in Diels-Alder reactions, tetrahydrofuran, dihydropyran and furoic acid [8]. Besides, FUR has been identified as a direct or indirect feedstock to more than 80 chemicals [9,10]. Consequently, FUR plays a major role as a platform molecule in future bio-refineries developments [1].

In the commercial process, FUR yield does not exceed 50 mol% and is associated with various environmental problems, such as toxic effluents derived from mineral acids (sulfuric or hydrochloric acid) and high energy demand due to the need of high temperatures of approximately 200 °C. In order to avoid the formation of high salt loads resulting from the neutralization of mineral acid catalysts, the development of easily-separable solid acid catalysts is being undertaken (e.g. zeolites [11-20], sulfonated graphenes [21-24], sulfated zirconia [6,25], alumina [26], coated activated carbon [15,27], among others [1]) and ionic liquids [5]. These recent advances suggest operational improvements involving green principles [28]. However, solid catalysts might face deactivation, fouling or low catalytical activity after the first cycle of reuse. Moreover, the unknown consequences of long-term use of ionic liquids, together with their elevated cost and yet inefficient recovery and recycling, set significant drawbacks to scale up their development [5].

In addition, the limited FUR yields are partly due to the formation of insoluble polymers (humins). These humins are decomposition products of both xylose and FUR, which react via resinification or condensation [1,29-32]. A recent article showed limited FUR yields of 49% in aqueous phase at 210 °C in 1 h using a xylose solution of 186 mmol L⁻¹ [33]. Several studies have suggested ways to inhibit the formation of humins and subsequently increase the FUR yield. One approach is to selectively extract the FUR instantaneously from the aqueous solution into an organic phase [34]. Trimble and Dunlop were the pioneers to implement this idea using ethyl acetate as the extracting media [35]. Subsequent research included studies on various organic solvents such as 2-sec-butylphenol, 4-n-hexylphenol, 2-methoxy-4-propylphenol [36], 1-butanol [37], γ -valerolactone [13,38], cyclohexanol [39], methyl isobutyl ketone (MIBK) [34,39], dimethyl sulfoxide (DMSO) [40,41], 1,3-Dimethyl-2-imidazolidinone (DMI) [42] and widely-used toluene [39]. However, most of these studies involve the addition of salts (used as phase modifiers) due to the high solubility of organic solvents in water, in order to increase the partition coefficient. Hence producing high salt waste after work-up, corrosion of the reactor and possible deactivation of acid sites on solid acid catalysts [43,44]. Besides, several solvents are toxic and are not ideal for industrial application. In contrast, green solvents from renewable sources such as 2-MTHF and CPME [45-47] are commercially available offering sustainable alternatives in order to extract FUR without the addition of salts due to its aqueous-immiscibility nature and provide a superior phase separation at the organic-water interface without forming emulsions [48]. An organic solvent with similar properties, isophorone, has been recently reported, which claims a higher distribution coefficient of FUR at 25 °C in a quaternary mixture of FUR+water+isophorone+acetic acid

(14) [49] than CPME (8.5) and 2-MTHF (8) [50]. Under normal conditions, isophorone has a solubility in water of 1.2 g/ 100 g at 20 °C [49], CPME of 1.1 g/ 100 g at 23 °C [47] and 2-MTHF of 14 g/ 100 g at 20 °C [51].

The aim of this work is to evaluate the production of FUR from xylose using a biphasic system including a novel promising water-immiscible solvent, isophorone, in which FUR is extracted thus increasing the FUR yield by reducing FUR decomposition reactions via condensation and resinification. The performance of isophorone is compared with other known water-immiscible organic solvents like CPME and 2-MTHF. An additional advantage of this system is the prevention of salt addition that offers a greener perspective in the FUR production. Furthermore, a liquid-liquid extraction (LLE) model was developed in order to predict the mass fractions of formed FUR in aqueous and organic phases under experimental conditions.

Experimental

Materials

D-Xylose powder (99%), isophorone, 2-MTHF and CPME were purchased from Sigma Aldrich.

D-Xylose powder was used in the experiments without further purification. Millipore grade water was used for preparing the solutions.

The birch hydrolysate was supplied by Stora Enso (Stora Enso, Imatra, Finland), which was used for the dehydration reaction experiments.

Methods

Xylose Dehydration Reaction Experiments in Biphasic System

Single containing D-xylose solution in a concentration typical for biomass hydrolysate (186 mmol l^{-1}) was freshly prepared before the experiments (Table A1 in the Supporting Information). These experiments can be considered as an auto-catalyzed reaction system where some side products (namely carboxylic acids) or intermediates, formed during the reaction, may have a catalytic effect [52,53]. In a typical experiment, the samples were prepared by heating 3 ml of an aqueous solution of 186 mmol l^{-1} xylose using a borosilicate glass reactor ($V = 10 \text{ cm}^3$) with magnetic stirring (600 min^{-1}), an irradiation power of $\leq 850 \text{ W}$ for maximum 2 min and microwave-assisted heating (Monowave 300, Anton Paar GmbH, Graz, Austria). The prepared solutions were tested for FUR yield, selectivity and xylose conversion at the reaction temperatures of 170, 190 and 210°C with different reaction times in the range of 30-240 min. The reaction vial was rapidly cooled after the reaction by compressed air inside the reactor until it reached 60°C . The highest temperature and the longest reaction time studied at the present work were 210°C and 180 min, respectively.

Birch Hydrolysate Dehydration Reaction Experiments in Biphasic System

The birch hydrolysate was filtered by using a glass filter with porosity 4 (Duran). The composition of the liquor was determined according to the analytical method NREL/TP-510-42623 [54]. The concentration of monomeric sugars was measured by high-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) by using a Dionex ICS-3000 column.

Determination of FUR and by-products

Samples for analysis were drawn from both the organic phase (top) and aqueous phase (bottom) after microwave heating. Xylose and FUR from aqueous phase were analyzed separately by High Performance Liquid Chromatography (HPLC) operating a Dionex UltiMate 3000 HPLC (Dionex, Sunnyvale, CA, USA) device equipped with refractive index (RI) and ultraviolet (UV) diode array detectors. Product separation was achieved on a HyperRez XP Carbohydrate Ca^+ column (Thermo Scientific, Waltham, MA, USA). Aqueous sulfuric acid (0.005 mol l^{-1}) was used as eluent with a flow rate of 0.8 ml min^{-1} . The column temperature and the RI-detector temperature were set to 70°C and 55°C , respectively. The FUR and hydroxymethylfurfural (HMF) concentration was determined by the UV-detector at a wavelength of 280 nm . The xylose concentration was analyzed simultaneously by the RI-detector and the UV-detector at 210 nm for a crosscheck [55]. FUR from the organic phase was analyzed by gas chromatography with a flame ionization detector (GC-FID) relative to iso-butanol as internal standard (IS). The column used was a DB-WAXetr (30 m , 0.32 mm i.d. , $1 \mu\text{m}$ film thickness) from Agilent Technologies Inc. The injected samples ($0.5 \mu\text{L}$) were subjected to a split ratio of 20:1 in the inlet maintained at 250°C and pressure of 12.967 psi . Helium was used as the carrier gas. The oven was initially maintained at 80°C for 1 min , after which the temperature was increased to 250°C at $30^\circ\text{C min}^{-1}$. The FID was operated at 250°C with hydrogen, air, and helium delivered at 30 ml min^{-1} , 380 ml min^{-1} , and 29 ml min^{-1} , respectively.

In this study conversion is defined in terms of moles of reactant converted per unit volume of reactor (eq. 1). Selectivity, at an instant, is the generated amount of moles of desired product referred to the moles of reactant converted (eq. 2). Yield is the amount in moles of desired product, FUR, produced relative to the amount of the key reactant, xylose (eq.

3) [56]. The following equations have been used for the mathematical evaluation of the obtained results:

$$X_{xyl} = \frac{c_{xyl}^{in} - c_{xyl}^f}{c_{xyl}^{in}} \times 100 [\%] \quad (\text{Eq. 1}),$$

$$S_{xyl}^{fur} = \frac{c_{fur}}{c_{xyl}^{in} - c_{xyl}^f} \times 100 [\%] \quad (\text{Eq. 2}),$$

$$Y_{fur} = \frac{c_{fur}}{c_{xyl}^{in}} \times 100 [\%] \quad (\text{Eq. 3}),$$

where X, S, Y are the— conversion of xylose, selectivity to FUR and FUR yield, respectively; *c* is the— concentration in mmol (the subscripts to be read as follows: *xyl*, *fur*, *in*, *f* are the— xylose, FUR, initial, final).

Furfural Decomposition Reaction Experiments in Biphasic System.

FUR decomposition reactions were conducted using a 10 ml borosilicate glass reactor with magnetic stirring (600 min⁻¹) and microwave-assisted heating (Monowave 300, Anton Paar GmbH, Graz, Austria). The vials were filled with 1.5 ml of 5 wt% FUR solution and 1.5 ml of the organic solvent. The prepared solutions in the biphasic system were tested for FUR concentration at the reaction temperatures of 170, 190 and 210 °C with different reaction times in the range of 30-180 min. The reaction vial was rapidly cooled down to 60 °C after the reaction via a stream of compressed air that was blown onto the reactor. Samples were stored at 0 °C until analyzed.

Results and Discussion

Furfural partitioning in a Biphasic Reactor System.

The partitioning of FUR in different organic solvents was investigated by conducting hydrothermal reactions wherein a solution of 5 wt% FUR in water was heated with isophorone, 2-MTHF, and CPME for 30 min at 190 °C at five different ratios of aqueous to organic solvent: 1:5, 1:2, 1:1, 2:1 and 5:1 (v/v). Figure 1 shows the FUR partition coefficients (P) obtained with the three organic solvents, where P was calculated using eq. 4 [39].

$$P = \frac{[FUR]_{org}}{[FUR]_{aq}} \quad (\text{Eq. 4})$$

A FUR partition coefficient of 9.1 was obtained with an aqueous to isophorone fraction ratio of 1:5. This value decreased to 7.5, 8.4, 6.9 and 6.6 as the aqueous to isophorone fraction ratio increased to 1:2, 1:1, 2:1 and 5:1, respectively. For 2-MTHF (4.6) and CPME (3.8) lower partition coefficients were obtained compared to isophorone.

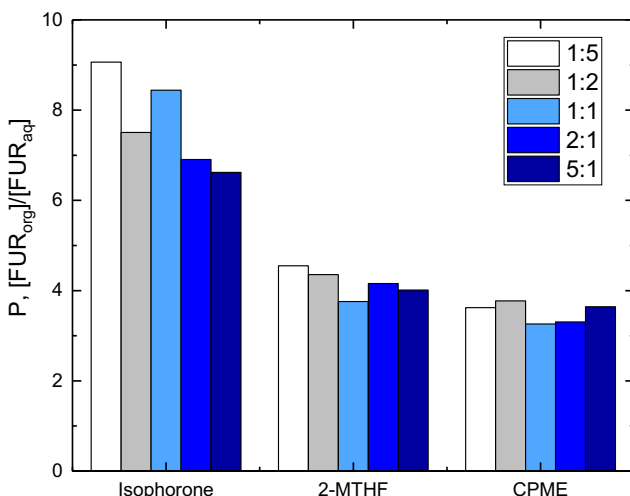


Figure 1. Partition coefficients for furfural among isophorone, 2-MTHF and CPME.

Partition coefficients were determined for a solution of 5 wt% furfural in water heated for 30 min at 190 °C (and then cooled down to 60 °C) at five different ratios of aqueous to organic solvent: 1:5, 1:2, 1:1, 2:1 and 5:1 (v/v).

In a recent article using isophorone [49], the partition coefficient of FUR in a ternary system was studied (FUR+isophorone+water). It can be observed that when the FUR fraction and temperature increase, the partition coefficient tends to decrease. However, under the experimental conditions of the present paper, the partition coefficient does not vary significantly (low mass fractions of FUR). Even though the partition coefficient of FUR when CPME and 2-MTHF tends to increase, when the FUR fraction and the temperature increase [57], its values do not vary significantly under the presented experimental conditions, due to the low mass fractions of FUR formed.

Furfural Production from Xylose

The effect of xylose dehydration on FUR production was studied in biphasic systems made with isophorone, 2-MTHF or CPME serving as the organic phase and an aqueous xylose solution.

Effect of organic phase and aqueous to organic phase ratio

Solubility of water in the organic solvents has been measured in recent papers for isophorone [49], 2-MTHF and CPME [57]. It is observed that solubility of water in the three organic solvents used in the present paper is minimal under the given experimental conditions.

The effect of different organic solvents and an aqueous solution of 186 mmol l⁻¹ was studied in biphasic systems at 190 °C in 30 min. For this, three water-immiscible solvents were studied: isophorone, 2-MTHF and CPME. Simultaneously, the effect of aqueous-to-organic phase ratio on xylose conversion and FUR production was investigated.

Consequently, five ratios of aqueous to organic phase (1:5, 1:2, 1:1, 2:1, 5:1; v/v) were planned. The FUR yields are shown in Figure 2 and are calculated using equation 3.

Figure 2 shows that the FUR yield increases as the aqueous to organic ratio increases from 1:5 up to 1:1 (v/v), regardless of the organic solvent. At ratios of aqueous to organic volumes of 2:1 to 5:1, we suggest that a higher FUR yield is prevented through the generation of increased decomposition products. The highest FUR yield (14%, Figure 2a) is reached (at 190 °C in 30 min) when employing isophorone in an aqueous to organic phase ratio of 1:1. When 2-MTHF is employed (Figure 2b), the highest FUR yield (13%) is also reached in an aqueous to organic phase ratio of 1:1. When CPME is used (Figure 2c), a FUR yield of 26% is reached at 190 °C in 30 min. Figure A1 (in the Supporting Information) displays the xylose conversion and the FUR selectivity in the three biphasic systems. When employing isophorone, the xylose conversion varied from 36% to 41%. When using 2-MTHF, xylose conversion varied from 40% to 44%; and CPME, where xylose conversion fluctuated from 41% to 56%. Selectivity to FUR increases as the aqueous to organic ratio increases from 1:5 to 1:1 (v/v), thereafter it decreases when increasing the aqueous to organic phase ratio to 5:1. The decrease of FUR selectivity could be due to saturation of the organic solvent to extract FUR.

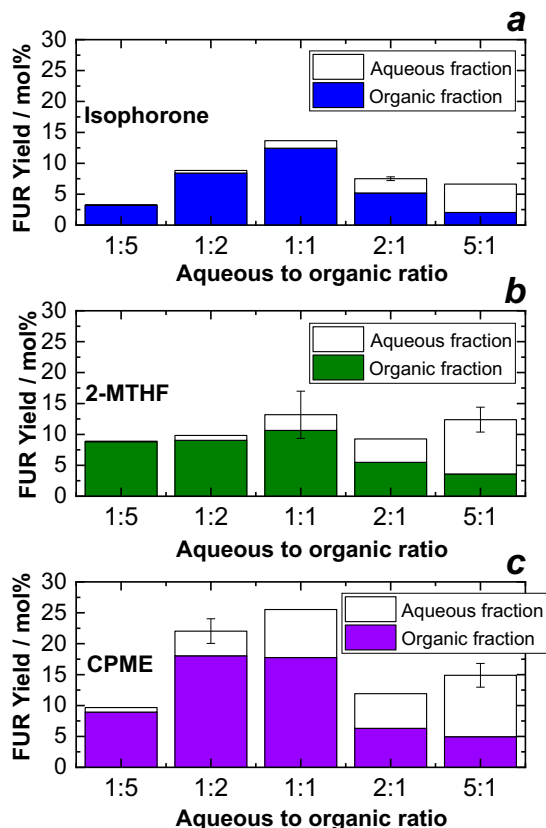


Figure 2. Effect of aqueous-to-organic ratio on FUR yield when using isophorone (a), 2-MTHF (b) and CPME (c) as organic phase. The effect was determined for a solution of xylose (186 mmol l^{-1}) heated at $190 \text{ }^{\circ}\text{C}$ in 30 min at five different ratios of aqueous to organic solvent: 1:5, 1:2, 1:1, 2:1, 5:1 (v/v). The error bars shown are one standard deviation from duplicate analyses.

Effect of reaction temperature

The influence of the reaction temperature on the dehydration of xylose and the resulting FUR yield was studied by using a 0.186 mol l^{-1} xylose concentration in a two-phase mixture at a temperature range between 100 and $200 \text{ }^{\circ}\text{C}$ for 30 min (water-organic solvent, 5:1 v/v) under microwave irradiation (Figure A2 in the Supporting Information). D-xylose is not soluble in the organic phase [49,57,58]. Thereby, the FUR yield varied

between 0 and 23 mol% (Fig. A2a). The effect of reaction temperature on FUR yield, xylose conversion and selectivity to FUR when working with an aqueous to organic ratio of 5:1 was further investigated. A low FUR yield was obtained from 100 to 150 °C (approximately 0%). The reason for lower FUR yield at the low reaction temperature was due to incomplete xylose conversion (below 15%, Fig. A2b). The highest FUR yield when employing CPME and 2-MTHF is 23% (at a xylose conversion of 57% and 49%, respectively) in 30 min at 200 °C, and when using isophorone is 18% (at a xylose conversion of 50%) at 200 °C (in 30 min).

Effect of reaction time

The effect of reaction time on the production of FUR was studied by conducting reactions between 30 to 180 min at 170, 190 and 210 °C with isophorone, 2-MTHF and CPME with a xylose solution of 186 mmol l⁻¹. Due to the low vapor pressure of 2-MTHF, reactions using this organic solvent at reaction temperatures of 210 °C were not possible to perform. Figure 3 shows the effect of reaction time when using CPME on FUR yield, xylose conversion and selectivity to FUR. In agreement with previous studies [59], FUR yield and xylose conversion were observed to be strongly influenced by the reaction temperature.

Figure 3 displays the effect of reaction time on FUR yield, xylose conversion and selectivity to FUR at 170, 190 and 210 °C when using CPME as organic solvent in an aqueous to organic phase ratio of 1:1. As seen in Figure 3a, after the first 60 min of the hydrothermal reaction the FUR yield was increased up to four times by increasing the temperature from 170 to 190 °C. The highest FUR yield (78%) was reached at 190 °C in

3 h. The maximum selectivity (Figure 3c) to FUR formation was 93%, 81% and 71% at temperatures of 170, 190 and 210 °C, respectively.

It can be seen, that at times longer than 120 min, the FUR yield obtained at 190 °C surpasses the FUR yield obtained at 210 °C. Under high reaction temperatures (210 °C) we assume that CPME does not extract FUR as efficiently. Therefore FUR tends to stay in the aqueous phase rather than in the organic phase, hence decomposition reactions of FUR occur faster.

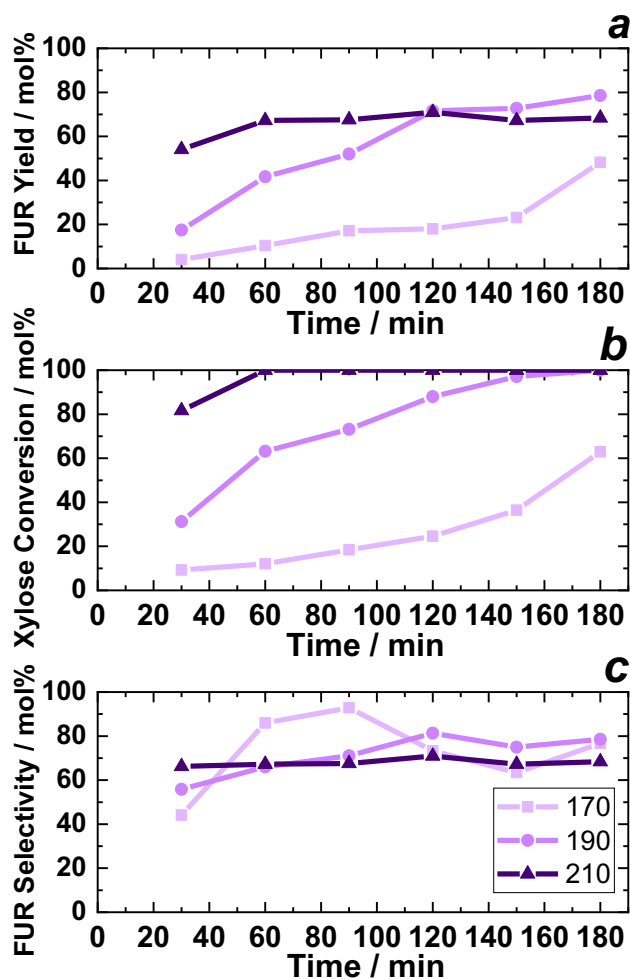


Figure 3. Effect of temperature and reaction time on (a) FUR yield, (b) xylose conversion, (c) selectivity to FUR in the dehydration of 28 g l⁻¹ xylose when using CPME as organic solvent with an aqueous to organic phase ratio of 1:1. Lines are to guide the eye.

When isophorone is used as water-immiscible solvent, the results are shown in Figure 4. For the first 60 min of the treatment the FUR yield was increased up to four times by increasing the temperature from 170 to 190 °C when employing isophorone to aqueous fraction ratio of 1:1 (Figure 4a). The highest FUR yield (49%) was reached at 190 °C in 3 h. The maximum selectivity (Figure 4c) to FUR formation was 48%, 54% and 43% at temperatures of 170, 190 and 210 °C, respectively. A similar phenomenon occurred when employing isophorone as observed with CPME. Under high reaction temperatures (210 °C), FUR tends to stay in the aqueous phase rather than in isophorone, hence decomposition of FUR occurs faster. In comparison to the performance of isophorone to 2-MTHF and CPME (Fig. 5), it might be that FUR enters the organic phase but undergoes degradation in the presence of the solubilized water within isophorone. Afterwards FUR precipitates out once a certain molecular weight is reached.

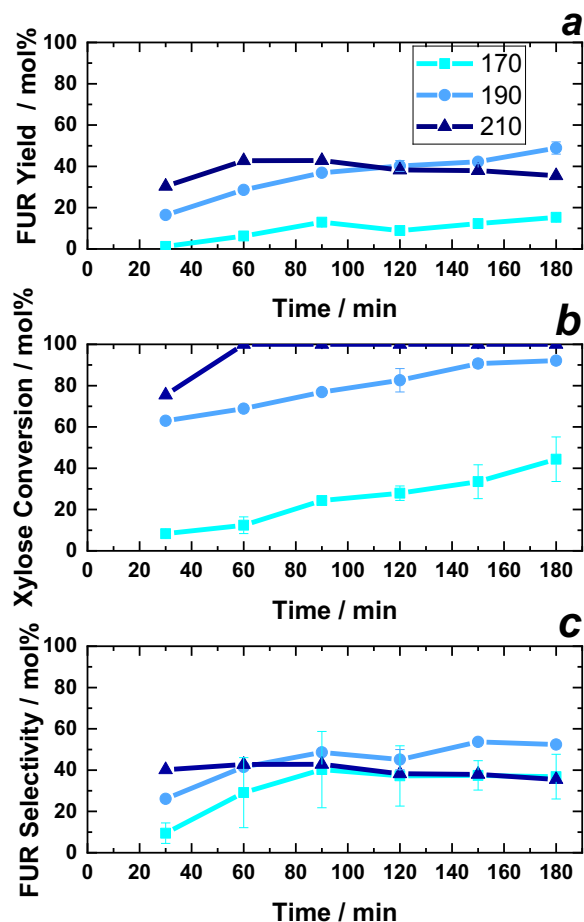


Figure 4. Effect of temperature and reaction time on (a) FUR yield, (b) xylose conversion, (c) selectivity to FUR in the dehydration of 186 mmol l⁻¹ xylose when using isophorone as organic solvent with an aqueous to organic phase ratio of 1:1. Lines are to guide the eye.

Figure 5 shows FUR yield, xylose conversion and selectivity to FUR when employing 2-MTHF. Figure 5a shows that the first 60 min of the treatment the FUR yield was increased up to two times by increasing the temperature from 170 to 190 °C when employing 2-MTHF to aqueous fraction ratio of 1:1. The highest FUR yield (71%) was reached at 190 °C in 3 h. The maximum selectivity (Figure 5c) to FUR formation was 58% and 80% at temperatures of 170 and 190 °C, respectively. Due to the low vapor pressure

of 2-MTHF, reactions using this organic solvent at reaction temperatures of 210 °C were not possible to perform.

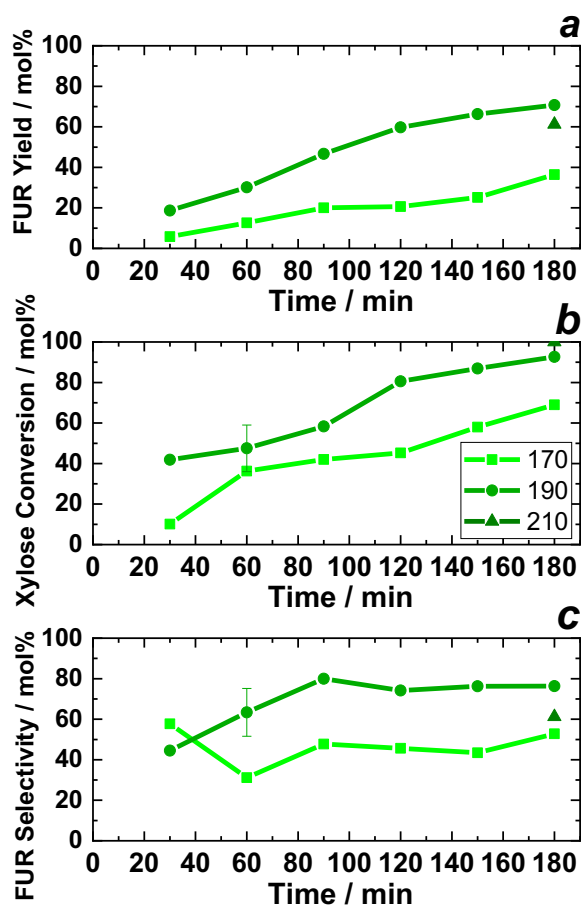


Figure 5. Effect of temperature and reaction time on (a) FUR yield, (b) xylose conversion, (c) selectivity to FUR in the dehydration of 186 mmol l⁻¹ xylose when using 2-MTHF as organic solvent with an aqueous to organic phase ratio of 1:1. Lines are to guide the eye.

Recent research of the auto-catalyzed system in aqueous phase has been published under similar experimental conditions [33,60]. The maximum FUR yield (48-49%) was reached at reaction temperatures of 210 °C and 220 °C in 1 h and 35 min, respectively, corresponding to a xylose conversion of 100% and 96%, respectively. It was observed that the FUR yield goes through a maximum and thereafter decreases with increasing

reaction time. Decrease of FUR yield is due to the condensation and resinification reactions that take place between FUR and xylose [29,31,32], producing humins, which are detrimental to FUR yield. In contrast, when using pure organic solvent, recent studies have shown low solubility of xylose in CPME [57,61]. Le Guenic et al recently reported [61] a limited selectivity to FUR (2%) after the reaction took place at 170 °C in 40 min when using only CPME in monophasic system.

Furfural decomposition in the biphasic system

To increase understanding of the behavior of FUR under the conditions of microwave-assisted reaction in the presence of an organic solvent, it is essential to know its degradation rate. The FUR degradation experiments were performed for the auto-catalyzed reactions using CPME and isophorone at the temperatures of 170, 190 and 210 °C. The experimental data showing the remaining fractions of FUR found in the aqueous and organic phases at various reaction times are presented in Fig. 6a and 6b, when adding isophorone and CPME, respectively. The figures illustrate the effect of the treatment temperature and the usage of 1:1 aqueous to organic phase ratio on the degradation rate of FUR. The results show a clear dependency of FUR degradation on the temperature, similarly to the data presented in earlier reports in monophasic systems [62-64]. It can be seen that when increasing the temperature the FUR degradation increases for both auto-catalyzed with isophorone and CPME. In addition, the results show that FUR is decomposed more rapidly in the presence of isophorone. The highest degree of degradation, 38%, was observed at 210 °C after 180 min. When CPME was employed as organic solvent, the highest degree of degradation was below 12%.

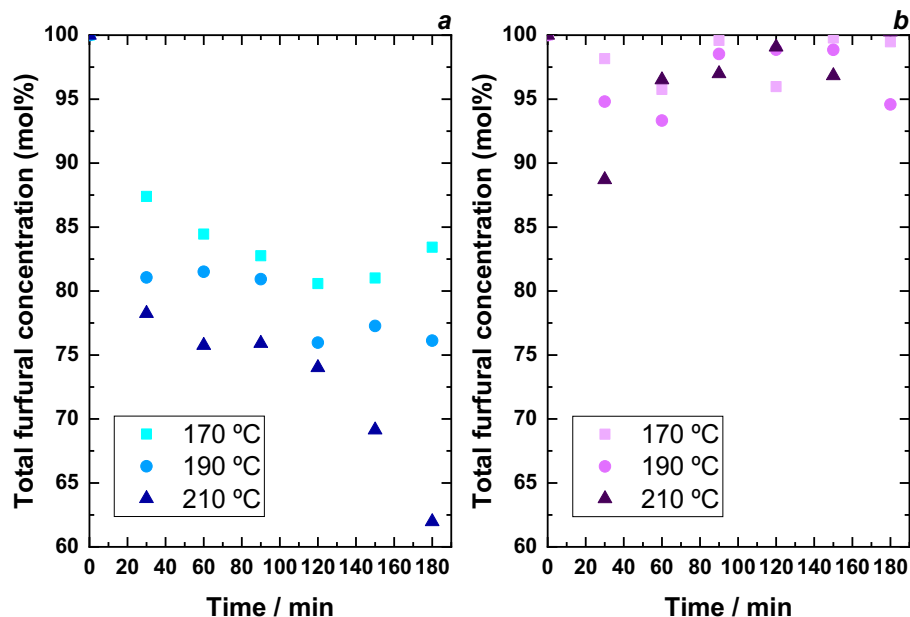


Figure 6. The remaining furfural at various reaction times during auto-catalyzed degradation when employing isophorone (a) and CPME (b) to aqueous phase of 1:1 (v/v). The decomposition of furfural was determined for a solution of 5 wt% furfural (squares – 170 °C, circles – 190 °C, triangle – 210 °C).

In order to confirm FUR decomposition in the presence of isophorone, a temperature level study was performed from 110 °C to 210 °C in 60 min when employing an aqueous to organic phase ratio of 1:1 (v/v). Fig. A3 (in the Supporting Information) shows that FUR decomposes linearly under the experimental conditions reaching the highest degree of degradation (24%) at 210 °C in 60 min.

Liquid-liquid equilibrium study

To get FUR from aqueous phase to organic phase the distribution should favor high solute distribution coefficients of FUR when defined as in Eq. (5)

$$K_i = \frac{w_{i,organic}}{w_{i,aqueous}} \quad (\text{Eq. 5})$$

where i refers to any component in the mixture. Isophorone-FUR-water data at 30, 50 and 70 °C was recently published by Ershova et al [49] demonstrating that at the equilibrium state the aqueous phase contains around 1 wt% isophorone and around 0.8–3.8 wt% FUR, whereas the organic phase contains 4.5–6.4 wt% water. In contrast, CPME-FUR-water and 2-MTHF-FUR-water at 20, 50 and 70 °C have been recently reported [57]. At the equilibrium state of 2-MTHF-FUR-water the aqueous phase contains from 1–11 wt% 2-MTHF and approximately 1–9.9 wt% FUR, while the organic phase contains 4.8–8.8 wt%. In the case of CPME-FUR-water the aqueous phase contains less than 1 wt% CPME and around 1.7–11 wt% FUR, whereas the organic phase contains 0.8–6 wt% water.

In order to confirm the values predicted by the LLE model, one test in each biphasic system was performed at 190 °C in 120 min (black dot). These tests show the consistency of the model in both aqueous and organic phase in the three biphasic systems. Even though when CPME and 2-MTHF are employed, FUR in the aqueous phase is not fully in line with predicted data, the values are comparable to the predicted data. This small deviation could be due to small droplets of organic solvent in the aqueous sample. Figures 7, 8 and 9 summarize the measured (dots) and predicted (lines) LLE phase equilibrium.

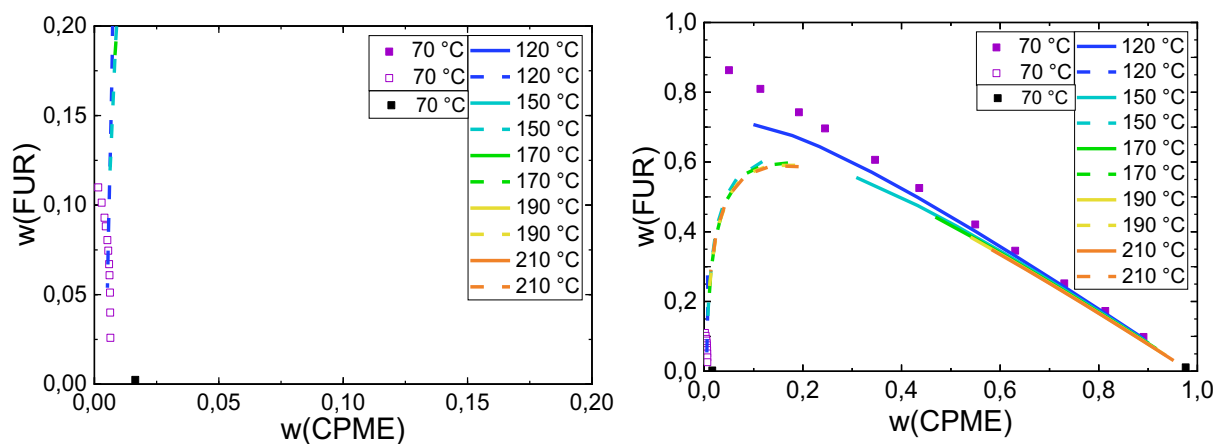


Figure 7. CPME and FUR binary LLE in mass fractions at atmospheric pressure. 70 °C Männistö et al., [50] 120-210 °C lines are extrapolated based on UNIQUAC model, filled symbol and solid line – organic (upper) phase, open symbol and dashed line – aqueous (lower) phase. Left figure shows the aqueous phase enlarged.

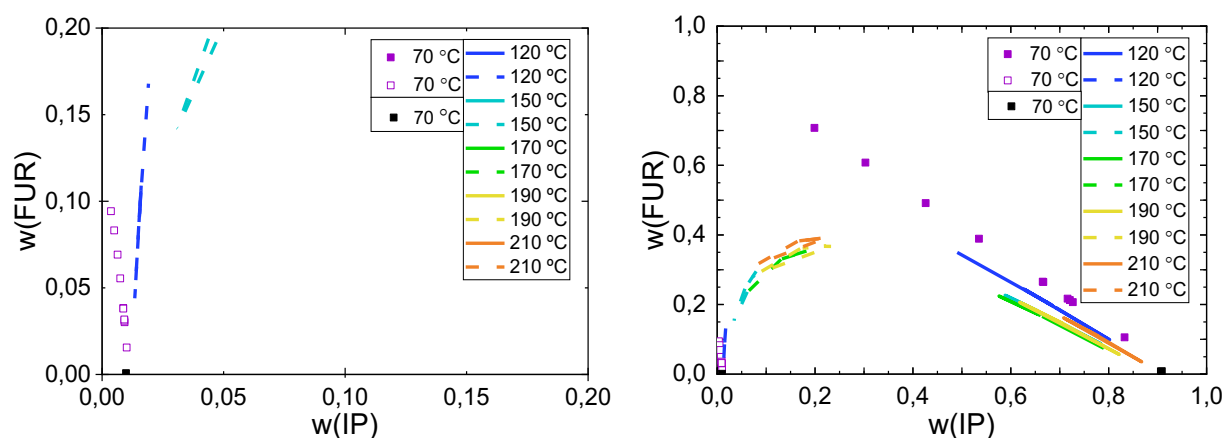


Figure 8. Isophorone (IP) and FUR binary LLE in mass fractions at atmospheric pressure. 70 °C symbols from Ershova et al. [49], 120-210 °C lines are extrapolated based on UNIQUAC model, filled symbol and solid line – organic (upper) phase, open symbol and dashed line – aqueous (lower) phase. Left figure shows the aqueous phase enlarged.

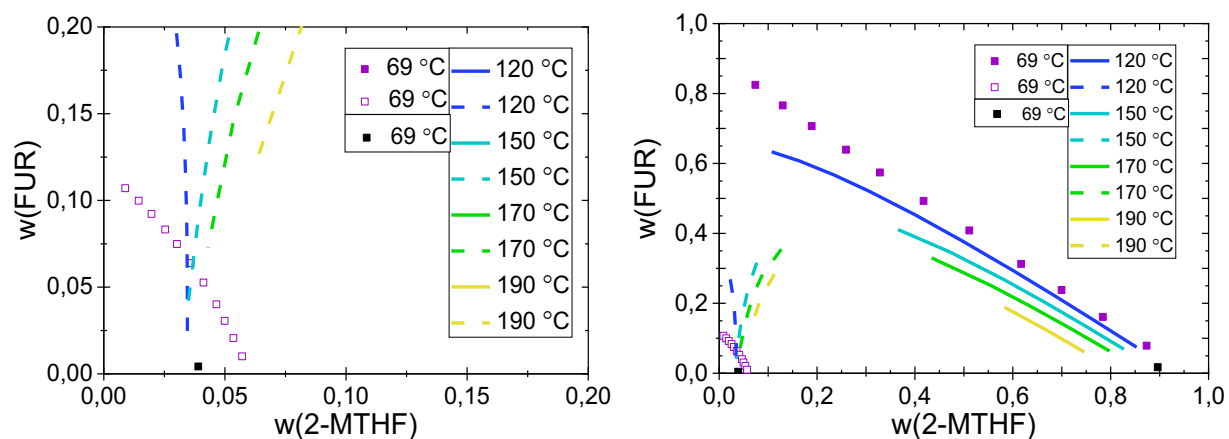


Figure 9. 2-MTHF and FUR binary LLE in mass fractions at atmospheric pressure. 70 °C symbols from Männistö et al. [50], 120-210 °C lines are extrapolated based on UNIQUAC model, filled symbol and solid line – organic (upper) phase, open symbol and dashed line – aqueous (lower) phase. Left figure shows the aqueous phase enlarged.

From the Figures 7-9 it can be seen that the slope of tie-line changes from positive to negative as temperature increases. It means that the distribution coefficient of FUR is higher than one close to room temperature but at the reaction temperature of this work it is less than one. The calculated distribution coefficients are presented in Figure 10.

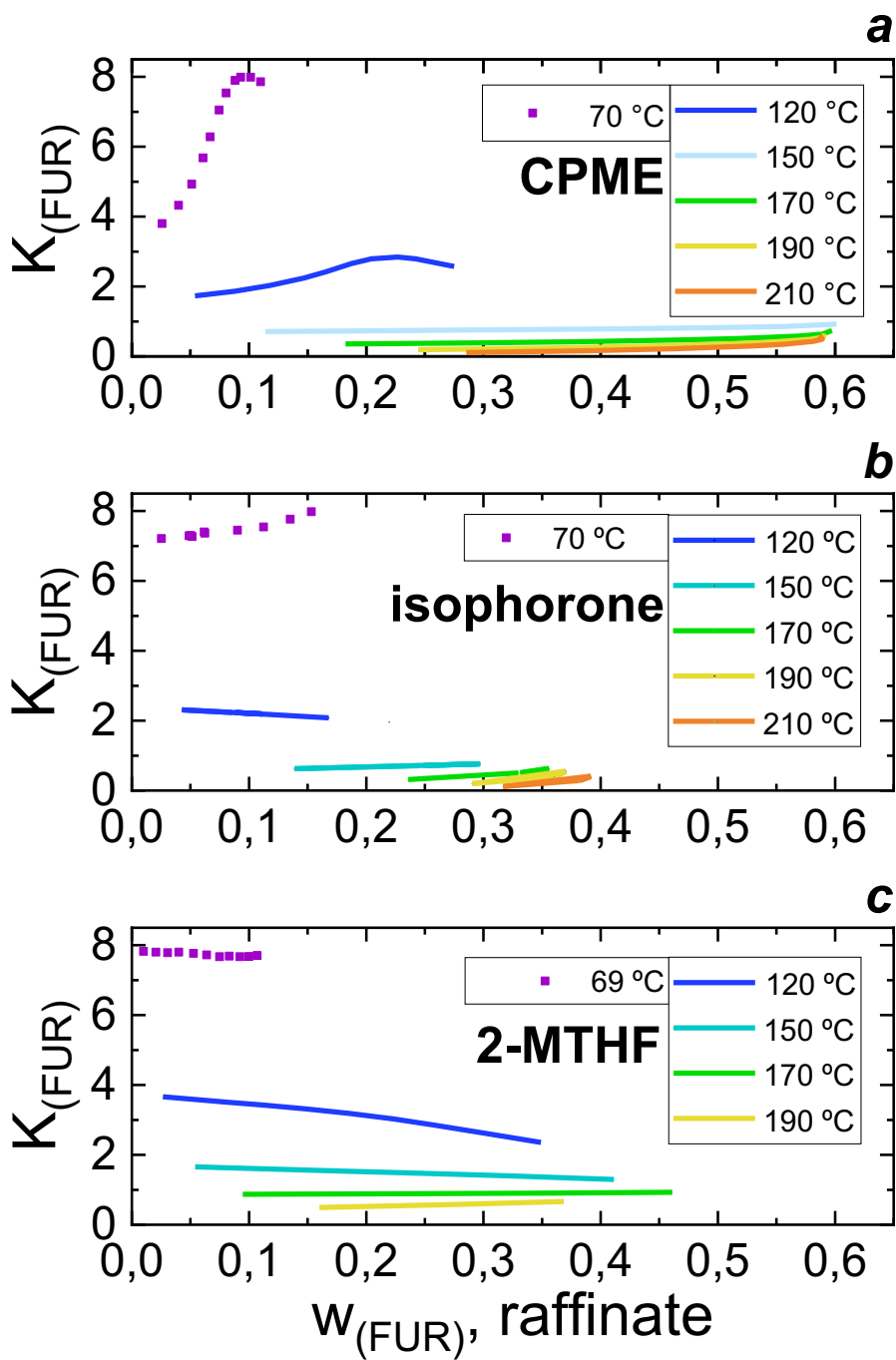


Figure 10. Distribution coefficient K for FUR in raffinate in the system when: a- CPME, b- isophorone and c- 2-MTHF are added to the system.

Based only on liquid-liquid equilibria (LLE) 2-MTHF gives K values of FUR higher than one at 150 °C but CPME and isophorone less than one. At 170 °C and higher temperature all solvents give the K-value of FUR less than one. In industrial practice, this could mean that lower temperatures are preferred for the FUR to be extracted adequately by the organic phase.

In the present work from the three water-immiscible organic solvents studied, isophorone shows a higher distribution coefficient of FUR, however CPME demonstrates a higher selectivity towards FUR without decomposition. This suggests that FUR undergoes decomposition reactions, potentially including isophorone as a co-reactant. Alternatively, the rate of degradation of FUR may be increased by an increasing content of water at temperatures approaching 200 °C. These possibilities were investigated by NMR analysis of the degradation of FUR: isophorone molar ratios of 1:1 and 1:10 at 190 °C over 30 min and 120 min (Figures A4-A6 in the Supporting Information). Potential mechanisms for this degradation might be, for example, Diels-Alder cycloaddition (isophorone as hindered dienophile), Aldol condensation (isophorone C6 reacting as nucleophile at the FUR aldehyde), Baylis-Hillman reaction (isophorone C2 reacting as nucleophile at the FUR aldehyde) and Michael addition (isophorone C3 as α - β unsaturated electrophile). Other reactivity may of course be possible [65-67].

Despite colourisation of the solutions after heating, ^1H NMR analysis (in DMSO - d_6 at 27 °C) showed that no new decomposition products were formed in significant quantities (Supporting Information Figures A7 and A8) and no precipitate was visible that might indicate significant condensation of FUR. Presence of water in the organic phase is another potential reason for losses of FUR. However, there is no literature LLE data

available for water and isophorone at the higher temperatures studied. The maximum temperatures quoted in the literature are only up to 70 °C [49]. The changing miscibility of water and isophorone up to 190 °C was crudely assessed by heating a mixture of isophorone (1 ml) and water (1 ml) in sealed narrow bore sample vials from 110 °C to 190 °C, with 5 min equilibration time every 10 °C (Figure A7 in the Supporting Information). At room temperature and even up to 110 °C the mixtures clearly form separate phases. However, as the temperature exceeds 150 °C the organic phase becomes cloudy, indicating dispersion of water into the phase. This phenomenon may be a result of increased hydrate (hemiketal) formation at the elevated temperatures or simply kinetic dispersion of clusters into the organic phase. These explanations, however, are speculative in the absence of accurate LLE data and require further studies to understand this phenomenon.

Further NMR experiments were also carried out after heating equivolume mixtures of FUR:H₂O, FUR:isophorone, FUR:H₂O:isophorone and Xylose:H₂O:isophorone at 210 °C for 3 h. The FUR:H₂O mixtures quickly degraded and formed a dark precipitate, from condensation of the FUR. All other mixtures coloured to some degree but did not form precipitate. The organic phases of each reaction were separated and evaporated to almost complete dryness by heating with a heat-gun (<150 °C) under oil pump vacuum with N₂ trap, to remove the majority of the volatiles (trace water, FUR or isophorone). The residues and also the solids from the FUR:H₂O mixture were added to DMSO-d₆ for NMR analysis. A multiplicity-edited HSQC and HSQC-TOCSY were recorded for the FUR:isophorone residue (Figure A8). This showed resonances characteristic of trace FUR and isophorone, in addition to several other low molecular weight decomposition

products or impurities. The main visible TOCSY correlations between the main aliphatic region (1-2.5 ppm in ^1H) and the FUR CH region (5.5-10 ppm in ^1H) seem to be between 2-CH and 3Cme or 4-CH₂ on isophorone, or related compounds. Thus, there does not seem to be any low molecular weight species that show obvious linkages between FUR and isophorone. However, this is not absolute proof that they do not exist and further inspection of the ^1H spectrum (Figure A9, top) shows that the low molecular weight aldehyde (CHO) functionalities are largely missing indicating potential linkage at the aldehyde functionality on FUR.

When a diffusion-edited ^1H experiment for the same sample is measured, compared to the standard ^1H experiment (Figure A9), it is clear to see that there is polymeric material in the DMSO-d₆ solution. Diffusion-editing has the effect of removal of the low molecular weight resonances and retention of the polymeric resonances [68]. The retained signals in the soluble organic fraction from the FUR:isophorone reaction correspond to both polymerised FUR and isophorone. Unfortunately, relaxation of these polymeric signals are too fast and abundances are too low so that we do not see the correlations to any significant degree, by HSQC or HSQC-TOCSY. Therefore, this makes it unclear if the FUR and isophorone-derived resonances are present due to co-precipitation or covalent linkage between the two moieties. If we compare the ^1H spectrum from the isolated solids from the FUR:H₂O reaction against the diffusion-edited ^1H spectra for the soluble fractions in the FUR:H₂O and FUR:isophorone reactions (Figure A10) it is clear that all mixtures contain polymeric material. In the case of the solids fraction from the FUR:H₂O reaction, the sample only partially dissolved in DMSO-d₆ indicating that there is a much higher molecular weight cross-linked polymer present. However, the spectrum looks very similar

to that of the soluble fraction of the corresponding FUR:H₂O reaction, except for the presence of the H₂O and DMSO peaks (standard ¹H experiment – not diffusion-edited). The diffusion-edited ¹H spectrum for the soluble organic fraction of the FUR:isophorone reaction contains a similar FUR CH region but is missing the aldehyde (CHO), likely attributable to the FUR aldehyde functionality on a polymerised furan backbone. In addition, there is the major contribution of the aliphatics, attributable to isophorone moieties. This might indicate that the aldehydes are an attachment point for isophorone to the polymerised furans. Reaction of isophorone at the aldehyde functionality of FUR is most likely via a Baylis-Hillman or Aldol type reaction. However, some isophorone 2-CH (5.8 ppm) is clearly still present in the polymeric fraction, so a combination of these and other possible mechanisms may be responsible.

When the diffusion-edited ¹H spectra for FUR:isophorone, FUR:H₂O:isophorone and Xylose:H₂O:isophorone are compared (Figure A11) we see some further changes from the inclusion of water with organics. The peak shape of the aliphatics change indicating new mechanisms of polymerisation. Aldehydes, FUR, CHs, isophorone, 2-CH and acetals are missing. However, this may be due to the formation of a rigid enough polymer backbone that the signals relax before the collection phase of the NMR experiments pulse sequence. Alternatively, a Diels-Alder-type or other cycloaddition reactions may be induced, which would lead to formation of aliphatic resonances. Water may have a significant effect here as formation of FUR hemiacetal would increase its reactivity, as a diene towards [4+2] cycloaddition, under the conventional Diels Alder HOMO-LUMO energy ordering. After all, water is well-known to have a rate-enhancing effect on the Diels-Alder reaction [69]. While this NMR result is inconclusive, clearly there is polymer

forming to some degree from polymerisation of FUR and/or isophorone in the presence of water.

While none of these NMR studies give measures of increased degradation of FUR, it shows that:

1. water does have a significant effect on the condensation of FUR [31,32]
2. isophorone may allow for increased miscibility with water at higher temperatures, which may lead to increased degradation kinetics of FUR
3. co-polymerisation of isophorone and FUR is likely occurring, which may lead to increased losses of both FUR and isophorone to some degree. This may be highly temperature dependent

Clearly more in-depth studies are required to isolate suitable polymeric fractions that might allow for more detailed NMR studies, to trace spin-systems between FUR and isophorone moieties, and to avoid the effects of transverse relaxation (T_2) which reduces the quantity of the diffusion-edited ^1H experiment.

Furfural production from birch hydrolysate

The production of FUR from birch hydrolysate was studied under optimized conditions for the dehydration of C_5 sugars (190 °C, 1:1 aqueous to CPME phase ratio, under microwave irradiation). The initial composition of the birch hydrolysate is given in Table A1 (in the Supporting Information).

The FUR yield increased from 37 mol% to 68% with an increasing time from 30 to 90 min at 190 °C when employing an aqueous to CPME phase ratio of 1:1 (Figure 11). The highest mole fraction of hydroxymethylfurfural (HMF) was 0.01 mmol (Figure A12 in the

Supporting Information), which is in agreement with previous studies when using birch hydrolysate to produce FUR from pentoses [70].

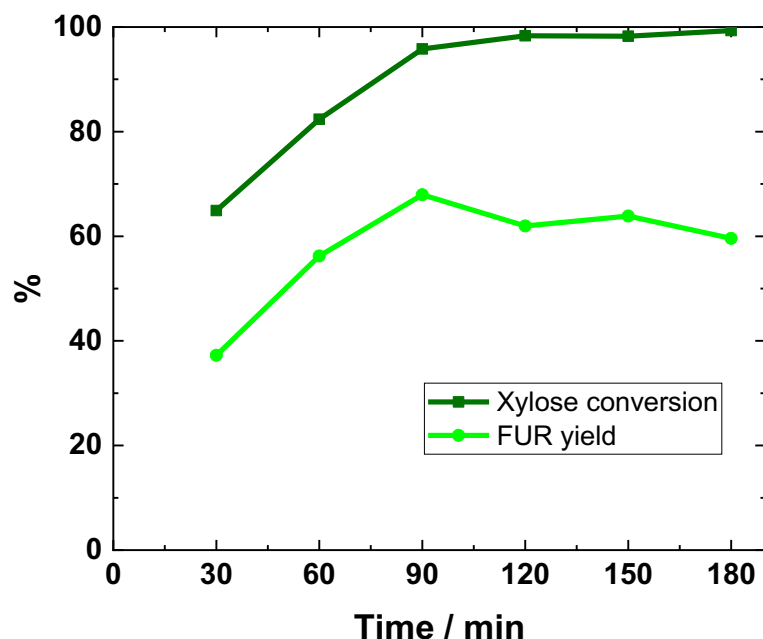


Figure 11. Xylose conversion and FUR yield from birch hydrolysate as a function of time at 190 °C under microwave irradiation. Biphasic reaction system: Aqueous phase = hydrolysate liquor after filtration (1.5 ml), organic phase: CPME (1.5 ml). The lines are to guide the eye.

Conclusion

In a two-phase system with three different water-immiscible organic solvents, the dehydration reaction of xylose and the resulting furfural yields were investigated under well-controlled conditions.

The optimum aqueous-to-organic phase ratio for all three tested organic solvents was 1:1 to extract FUR in the dehydration of xylose. The main product of auto-catalyzed and solid acid-catalyzed xylose dehydration was FUR, whose maximum mole fraction yield at 190

°C in 180 min was 78% in the case of CPME as an organic solvent phase. The highest selectivity to FUR, namely 93%, was achieved in 90 min at 170 °C when CPME was added.

In the case of birch hydrolysate as pentose source, a maximum FUR yield of 68% (and a xylose conversion of 96%) after 90 min autocatalyzed reaction at 190 °C was achieved under the optimized conditions of a two-phase dehydration reaction in the presence of CPME in a volume ratio of 1:1.

The results of the experiments when using isophorone as organic solvent allowed us to conclude that there are decomposition reactions between the solvent and FUR above 110 °C, which may or may not be linked to an increase on water solubility at elevated temperatures. Therefore, even though isophorone shows a higher partition coefficient in the biphasic system, it should be employed at temperatures below the conditions stated in the present study.

Studies on the in-situ extraction of FUR involving with solvents that are not miscible with water show a high selectivity to FUR and thus increase its yield. This offers an interesting approach for a greener process and the avoidance of salt addition.

Acknowledgements

This research has been done in collaboration with Stora Enso and funded through Erasmus Mundus Joint Doctoral Programme SELECT+, the support of which is gratefully acknowledged. G.G.M. was supported also by CONACyT-SENER-Sustentabilidad Energética 2016 (the Mexican National Council of Science and Technology-Secretariat of Energy-Sustainable Energy 2016).The authors are also grateful for the support of the staff at the Department of Bioproducts and Biosystems at Aalto University especially to

Heidi Meriö-Talvio and Mika Sipponen. JL is a Serra Húnter Fellow and is grateful to ICREA Academia program.

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